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(54) **Abradable quasicrystalline coating**

(57) A thermally sprayed coating formed with a quasicrystal-containing alloy, the alloy consisting essentially of, by weight percent, 10 to 45 Cu, about 7 to 22 Fe, 0 to 30 Cr, 0 to 30 Co, 0 to 20 Ni, 0 to 10 Mo, 0 to 7.5 W and balance aluminum with incidental impurities. The alloy contains less than 30 weight percent  $\psi$  phase and at least 65 weight percent  $\delta$  phase. The coating has a macrohardness of less than HR15Y 90.

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## Description

BACKGROUND OF THE INVENTION5 FIELD OF THE INVENTION

[0001] The present invention relates to aluminum-copper-iron quasicrystal alloys and in particular abrasion-resistant quasicrystal coatings that exhibit low-friction properties.

10 DESCRIPTION OF RELATED ART

[0002] Quasicrystals are materials whose structure cannot be understood within classic crystallographic methodology. These quasiperiodic structures have a long-range orientation order, but lack translational periodicity. Conventional crystals consist of repeated copies of a single geometric atomic arrangement—a unit-cell stacked upon each other like bricks. Quasicrystals, on the other hand, while also being built up from a single type of atomic clusters, differ in that adjacent clusters overlap, sharing atoms with their neighbors. When clusters overlap by sharing atoms (quasiperiodic packing), they produce denser atomic arrays than conventional, periodic, repeated packing patterns.

[0003] The non-periodic structure of Quasicrystals yields a broad, previously unobtainable range of physical properties embodied within a single material. Quasicrystals exhibit poor thermal conductivity while remaining stable up to about 1100°C. Thus, a thin layer on a heat-conducting surface will distribute heat evenly eliminating "hot spots". These hard coatings promote wear and scratch resistance. Furthermore, due to their low coefficient of friction and electronic structure (low surface energy), they possess non-adhesive properties. Finally, they offer resistance to both corrosion and oxidation.

[0004] Researchers have identified over eight hundred different quasicrystal alloys. Many of these alloys contain a combination of aluminum, copper and iron. The Al-Cu-Fe alloys yield the specific icosahedral quasicrystal identified in atomic percent as  $Al_{65}Cu_{20}Fe_{15}$ . (Note: This specification expresses all composition in weight percent, unless specifically noted otherwise). Furthermore, in some instances these alloys contain additional alloying elements such as, chromium, cobalt and nickel. This enables the alloy to accommodate specific operating conditions. For example, DuBois et al., in U.S. Pat. No. 5,204,191, describe several Al-Cu-Fe alloys containing quasi-crystalline phases.

[0005] Regardless of chemistry however, quasicrystals do not lend themselves to conventional fabrication. They can not be formed or readily cast; however, they can be reduced to powder and thermally sprayed to form an adherent, useful coating. As far as known however, none of these alloys have established widespread commercial usage.

[0006] It is an object of this invention to produce an Al-Cu-Fe quasicrystal alloy coating having decreased hardness for improved abrasion resistance.

[0007] It is a further object of this invention to produce an abrasion-resistant Al-Cu-Fe quasicrystal alloy coating having high temperature stability and oxidation resistance.

SUMMARY OF THE INVENTION

[0008] A thermally sprayed coating formed with a quasicrystal-containing alloy, the alloy consisting essentially of, by weight percent, 10 to 45 Cu, 7 to 22 Fe, 0 to 30 Cr, 0 to 30 Co, 0 to 20 Ni, about 0 to 10 Mo, 0 to 7.5 W and balance aluminum with incidental impurities. The alloy contains less than 30 weight percent  $\psi$  phase and at least 65 weight percent  $\delta$  phase. The coating has a macrohardness of less than HR15Y 90.

45 DESCRIPTION OF PREFERRED EMBODIMENT

[0009] The coating consists of a wear resistant Al-Cu-Fe alloy having less than about 30 weight percent  $\psi$  phase and at least about 65 weight percent  $\delta$  phase thermally sprayed at a subsonic rate sufficient to avoid excessive quantities of the hard  $\psi$  phase. Advantageously, the alloy contains at least about 70 weight percent  $\delta$  phase. Most advantageously, this alloy contains less than about 10 weight percent  $\psi$  phase and at least about 80 weight percent  $\delta$  phase. The thermally sprayed coating possesses excellent abrasion resistance and bond strength. Advantageously, the coating has a bond strength of at least about 7 MPa (1 ksi). Furthermore, this quasicrystalline alloy contains chromium or cobalt for corrosion resistance.

[0010] Aluminum, copper, iron and chromium were vacuum melted and inert gas atomized. The powder analyzed, by weight percent, 17.5 Cu, 13.3 Fe, 15.3 Cr and balance aluminum. This powder was fully spherical and free flowing. Table 1 lists typical properties of the inert gas atomized AlCuFeCr quasicrystal powder after sizing.

Table 1

Size	+75 $\mu\text{m}$	0.02%
	+63 $\mu\text{m}$	5.40%
	-63 $\mu\text{m}$	94.58%
Apparent Density	2.14 g/cm <sup>3</sup>	
Flow Rate (ASTM B213)	30 Seconds	

[0011] Due to the alloy's aperiodic lattice structure, x-ray diffraction (XRD) identified the quasicrystals. The positions of the quasicrystal or (icosahedral ( $\psi$ )) phase are roughly at 23, 25, 41, 44, 62.5, and 75--an icosahedral is a polygon having 20 faces and a decagon is a polygon having 10 angles and 10 faces. As-atomized, sized powder showed only a minor amount of  $\psi$  phase. Rather, a decagonal phase ( $\delta$ ) predominated. The presence of two (2) phases was attributed to the rate of cooling experienced in going from liquid to solid. Cooling rate, and subsequent powder particle solidification, greatly affected resulting phase equilibria. At very fast rates the metastable  $\psi$  is formed; if solidification is slowed the  $\delta$ -phase or its approximates form. Differential thermal analysis (DTA) performed on the powder indicated a melting temperature of about 1044°C.

[0012] When reduced to powder, these quasicrystals facilitate thermal spraying with various types of equipment. This includes plasma, HVOF, detonation and other types of thermal spraying equipment. However, for this example plasma was selected as the sole means of application. The equipment used to apply the coatings was the Praxair SG-100 plasma gun. The gun was mounted onto an ABB IRB 2400 robot's arm to facilitate automatic spraying and to ensure consistency. The plasma generator was configured to operate in the sub-sonic mode. Utilized hardware is recorded in Table 2.

Table 2

Anode	2083-155
Cathode	1083A-112
Gas Injector	3083-113
External Powder Feed	Negative

[0013] The subsonic coatings were applied to and evaluated for macrohardness (HR15Y); microstructure, including density and oxide content as determined using image analysis; surface roughness; XRD for phase distribution; and tensile/bond testing. Based upon macrohardness and bond strength an optimized set of spray parameters was derived. Along with gun traverse rate, the six active and controllable parameters were given high and low ranges. Table 3 illustrates the controlled parameters.

Table 3

Amps A	600	650	700
2ndary B	15 l/min	20 l/min	25 l/min
Primary C	32.8 l/min	37.7 l/min	42.8 l/min
Feed Rate D	30 g/min	45 g/min	60g/min
Distance E	64 mm	76 mm	89 mm
Traverse F	250 cm/min	305 cm/min	355 cm/min

[0014] Coatings from the subsonic coating yielded a HR15Y distribution ranging from 81.6 to 85.8. Constructing a Response Table, parameters were calculated for two (2) coatings - one for each end of the hardness spectrum. Predicted hardnesses were 81.5 (low) and 86.5 (high). Both parameter sets were sprayed; results are found in Table 4.

Table 4

	Soft	Softer
Amperage	650	600
Secondary (H <sub>2</sub> )	3.5 l/min	2.35 l/min
Primary (Ar)	48.37 l/min	56.6 l/min
Feed Rate	30 g/min	60 g/min
Carrier Gas (Ar)	4.1 l/min	4.1 l/min
Spray Distance	76 mm	64 mm
Traverse Rate	305 cm/min	250 cm/min

**[0015]** Table 5 below illustrates the excellent abrasable properties achieved with the subsonic thermal spraying of the quasicrystalline alloy.

Table 5

	Soft	Softer
HR15Y	86.5	83.6
Density	95.0%	84.0%
Bond Strength	18.89 MPa	12.63 MPa
Deposit Efficiency	35%	25%

**[0016]** Based upon the porous nature of these subsonic coatings there were no attempts to perform microhardness testing. XRD scans on the two subsonic coatings appear similar, almost a "look alike" of the starting powder. Both coatings are predominately  $\delta$  with a weak  $\psi$  peak at 42. The metallography of the coating illustrated the presence of transplat cracking.

**[0017]** Table 6 below provides "about" the thermally sprayed coating's composition, in weight percent.

Table 6

Element	Broad	Intermediate	Narrow
Al	Balance*	Balance*	Balance*
Cu	10 - 45	12 - 24	15 - 20
Fe	7 - 22	10 - 20	10 - 16
Cr	0 - 30	5 - 25**	10 - 20
Co	0 - 30	0 - 20**	0 - 15
Ni	0 - 20	0 - 15	0 - 10
Mo	0 - 10	0 - 7.5	0 - 5
W	0 - 7.5	0 - 6	0 - 5

\* Plus incidental impurities.

\*\* Cr + Co is at least 10.

**[0018]** The hardness and bond strength properties initially targeted for modification were appreciably improved. For example, hardness improved from HR15N levels for conventional thermal spraying to a level of less than about HR15Y 90. Advantageously, the alloy has a hardness of less than about HR15Y 85. Most advantageously, the alloy has a hard-

ness of about HR15Y 65 to 85. Quasicrystals have very poor thermal conductivity and therefore any level of inputted thermal energy should be considered when spraying.

[0019] These "soft" quasicrystal coatings provide excellent abradable thermal barrier underlayments. Furthermore, it is possible to improve abradability and lubricity with additions of polymers (such as, nylon, polyamides and polyesters), boron nitride, clad boron nitride (nickel or chromium) and nickel-coated graphite.

[0020] The coating retains at least 65 weight percent  $\delta$  phase and limits  $\psi$  phase to less than 30 weight percent to ensure a soft abradable alloy. This coating may be sprayed onto either metallic or non-metallic substrates. Finally, the quasicrystalline alloy readily incorporates chromium and cobalt additions for improved high temperature oxidation resistance.

[0021] Although the invention has been described in detail with reference to a certain preferred embodiment, those skilled in the art will recognize that there are other embodiments of the invention within the spirit and the scope of the claims.

## Claims

1. A thermally sprayed coating formed with a quasicrystal-containing alloy, the alloy consisting essentially of, by weight percent, about 10 to 45 Cu, about 7 to 22 Fe, about 0 to 30 Cr, about 0 to 30 Co, about 0 to 20 Ni, about 0 to 10 Mo, about 0 to 7.5 W and balance aluminum with incidental impurities and having less than about 30 weight percent  $\psi$  phase and at least about 65 weight percent  $\delta$  phase and the coating having a macrohardness of less than about HR15Y 90.
2. The coating of claim 1 wherein the coating has a macrohardness of less than about HR15Y 85.
3. The coating of claim 1 wherein the alloy contains at least about 70 weight percent  $\delta$  phases.
4. The coating of claim 1 wherein the coating contains soft particles selected from the group consisting of polymers, boron nitride, clad boron nitride, and nickel-coated graphite.
5. A thermally sprayed coating formed with a quasicrystal-containing alloy, the alloy consisting essentially of, by weight percent, about 12 to 24 Cu, about 10 to 20 Fe, about 5 to 25 Cr, about 0 to 20 Co, at least about 10 total Cr and Co, about 0 to 15 Ni, about 0 to 7.5 Mo, about 0 to 6 W and balance aluminum with incidental impurities and having less than about 30 weight percent  $\psi$  phase and at least about 65 weight percent  $\delta$  phase and the coating having a macrohardness of less than about HR15Y 90.
6. The coating of claim 5 wherein the coating has a macrohardness of less than about HR15Y 85 and the alloy contains at least about 70 weight percent  $\delta$  phase.
7. The coating of claim 5 wherein the coating contains soft particles selected from the group consisting of polymers, boron nitride, clad boron nitride and nickel-coated graphite.
8. A thermally sprayed coating formed with a quasicrystal-containing alloy, the alloy consisting essentially of, by weight percent, about 15 to 20 Cu, about 10 to 16 Fe, about 10 to 20 Cr, about 0 to 10 Co, about 0 to 10 Ni, about 0 to 5 Mo, about 0 to 5 W and balance aluminum with incidental impurities and having less than about 30 weight percent  $\psi$  phase and at least about 65 weight percent  $\delta$  phase and the coating having a macrohardness of less than about HR15Y 90.
9. The coating of claim 8 wherein the coating has a macrohardness of about HR15Y 65 to 85 and the alloy contains less than 10 weight percent  $\psi$  phase and at least about 80 weight percent  $\delta$  phase.
10. The coating of claim 9 wherein the coating contains soft particles selected from the group consisting of polymers, boron nitride, clad boron nitride and nickel-coated graphite.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 10 5404

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL7)
A	CHEMICAL ABSTRACTS, vol. 128, no. 24, 15 June 1998 (1998-06-15) Columbus, Ohio, US; abstract no. 297907, HOLLAND-MORITZ, D. ET AL: "Undercooling and solidification behavior of melts of the quasicrystal-forming alloys Al-Cu-Fe and Al-Cu-Co" XP002141897 * abstract * & ACTA MATER. (1998), 46(5), 1601-1615 , 1998,	1,8	C23C4/06 C23C4/12
A	FR 2 685 349 A (CENTRE NAT RECH SCIENT) 25 June 1993 (1993-06-25) -----		
			TECHNICAL FIELDS SEARCHED (Int.CL7)
			C23C
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>5 July 2000</b>	Examiner <b>Gregg, N</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... &amp; : member of the same patent family, corresponding document</p>			

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ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 00 10 5404

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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05-07-2000

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
FR 2685349     A	25-06-1993	CA     2106399 A	21-06-1993
		DE     69209057 D	18-04-1996
		DE     69209057 T	02-10-1996
		EP     0572646 A	08-12-1993
		WO     9313237 A	08-07-1993
		JP     6505773 T	30-06-1994
		US     5571344 A	05-11-1996
		US     5649282 A	15-07-1997
		US     5888661 A	30-03-1999
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